

On the determination and simulation of seawater freezing point temperature under high pressure

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Abstract At present, it is believed that the freezing point temperature of seawater is a function of salinity and pressure, and the freezing point is a key parameter in a coupled air-sea-ice system. Generally, empirical formulas or methods are used to calculate the freezing point of seawater. Especially in high-pressure situations, e.g., under a thick ice sheet or ice shelf, the pressure term must be taken into account in the determination of seawater freezing point temperature. This study summarized various methods that have been used to calculate seawater freezing point with high pressure. The methods that were employed in two ocean-ice models were also assessed. We identified the disadvantages of these methods used in these two models and addressed the corresponding uncertainties of the freezing point temperature formulas. This study provides useful information on the calculation of the freezing point temperature in numerical modeling and indicates a need to investigate the sensitivity of numerical simulations to the uncertainties in the freezing point temperature in future.

Keywords freezing point temperature, seawater, salinity, pressure, comparison

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1 Introduction

The temperature at the transition point between liquid and solid water is defined as the freezing point temperature, or more simply the freezing point. Pure water becomes frozen when the temperature drops to 0.002519 °C at normal pressure (101325 Pa) (Feistel and Wagner, 2006). However, the freezing point of seawater is lower than that of fresh water. When the surface water of the ocean approaches the freezing point, the density of seawater increases and hence tends to sink, usually leading to vertical convection and mixing, unlike the situation of fresh water. Also, the freezing of seawater precipitates ice mixed with brine in a slush, which leads after its flushing to an increase in salinity

under the ice and hence further drops the freezing point of the adjacent seawater (Brennecke, 1921; Seabrooke et al., 1971). And the freezing point of seawater decreases with the increase of salinity and pressure in the form of a weak nonlinear function of salinity and a linear function of pressure (Millero, 1978).

The freezing point of seawater under high pressure is a key parameter in the interactions between ice and ocean, particularly at the base of ice shelves near the grounding line. The accuracy of the freezing point calculation has an important influence on the simulation of melting/freezing of ice in the ocean and hence fresh water budget, and on other processes. Modeling studies often use a linear function of salinity and pressure to approximate the freezing point, e.g., Massachusetts Institute of Technology General Circulation Model (MITgcm) (Marshall et al., 1997) and Regional Ocean

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Model System (ROMs) (Shchepetkin and McWilliams, 2005; Haidvogel et al., 2008; Shchepetkin and McWilliams, 2009). However, in some areas of high pressure, it is not clear how much error the current formulas create—the subject has not been studied.

The paper is organized as follows. Section 2 provides a summary of the methods for determining the freezing point of seawater. Section 3 describes the freezing point formulas used in the simulations of MITgcm and ROMs. Section 4 compares and discusses the differences of various calculation methods. Section 5 concludes with a brief summary of our results.

2 The methods for determining the freezing point of seawater

2.1 The relationship between freezing point and salinity at constant pressure

Tamman (1900) had studied the temperature of the freezing point under high pressure, by conducting an experiment in the laboratory (Henderson and Speedy, 1987).

Knudsen(1903) measured the freezing point of seawater by experiment, and obtained the following empirical formula,

$$T_f = -0.0086(^{\circ}\text{C}) - 0.064633(^{\circ}\text{C}) \sigma_0 - 0.0001055(^{\circ}\text{C}) \sigma_0^2, \quad (1)$$

where T_f is the freezing point, $\sigma_0 = (S_0 - 1) \times 1000$ (S_0 is the density of seawater at 0 °C divided by the density of distilled water at 4 °C, namely, the specific gravity of seawater at 0 °C), and the value of σ_0 is from the density work of Knudsen (1902).

Based on the Knudsen-Hansen freezing point formula, Thomas and Thompson (1932) deduced the relationship between the freezing point of seawater and the concentration of chlorine (Miyake, 1939),

$$T_f = -0.0966(^{\circ}\text{C})Cl - 0.00000520(^{\circ}\text{C})Cl^3, \quad (2)$$

where Cl is chlorinity of seawater (it is the total grams of chlorine in 1 kg of seawater after the replacement of bromine and iodine by equivalent chlorine).

Miyake et al. (1939) found a linear relationship between the depression of the temperature of seawater freezing point and the chlorine (see Figure 1) by repeating the experiment of seawater freezing point (Figure 2, point C is considered to be the freezing point). The expression is as follows:

$$\Delta T = 0.102710(^{\circ}\text{C})Cl \quad (3)$$

In this experiment, seawater was diluted with water to obtain six samples with differing amounts of chlorine. ΔT , the depression of the freezing point of seawater was given by the difference between the result of a sample and that of the standard, distilled water. Also, this empirical formula for the freezing point of seawater is only a function of salinity, without the influences of pressure.

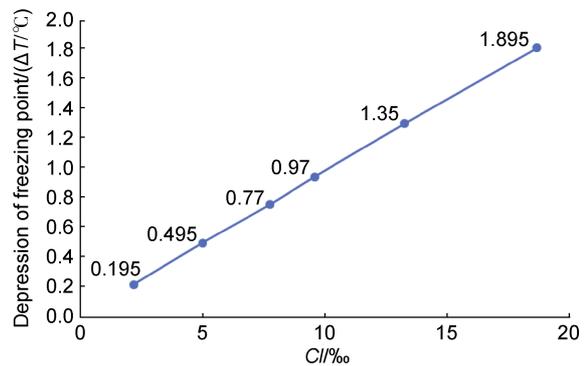


Figure 1 The relationship between the depression of the temperature of seawater freezing point and the chlorine concentration, determined by Miyake et al. (1939).

Fujino et al. (1974) added strong mixing. During the freezing and melting phases of the supercooled cycle, the same freezing point was then observed under the same salinity condition (Figure 2, near point D). The salinity ranged from 17.7‰ to 35‰, and the relationship between the freezing point temperature and salinity at atmospheric pressure was determined as:

$$T_f = -0.036(^{\circ}\text{C}) - 0.0499 \left(\frac{^{\circ}\text{C}}{\text{psu}} \right) S - 0.000112 \left(\frac{^{\circ}\text{C}}{\text{psu}^2} \right) S^2, \quad (4)$$

(17.7‰ < S < 35‰)

where S is salinity, the ratio of all dissolved solids in seawater to the weight of seawater. In oceanography, the standard unit for salinity is now psu (practical salinity unit), which is a dimensionless unit and expressed as ‰. On average, ocean salinity is 35‰.

Doherty and Kester (1974) measured the freezing point through three methods: supercooling, flow and equilibrium, when salinity varies from 3.8‰ to 40.2‰ (Doherty and Kester, 1974). They obtained the following formula at one standard atmospheric pressure:

$$T_f = -0.0137 - 0.051990 \left(\frac{^{\circ}\text{C}}{\text{psu}} \right) S - 0.00007225 \left(\frac{^{\circ}\text{C}}{\text{psu}^2} \right)^2, \quad (5)$$

(3.8‰ < S < 40.2‰)

This formula used a wider range of salinity (3.8‰ < S < 40.2‰) than that of Fujino et al. (1974) (17.7‰ < S < 35‰). Fujino et al. (1974) and Doherty and Kester (1974) also measured the effect of pressure on the freezing point, which will be discussed in the next section.

2.2 The relationship between freezing point of seawater and pressure

At present, the relationship between the freezing point of seawater and pressure is established by experiment, or by

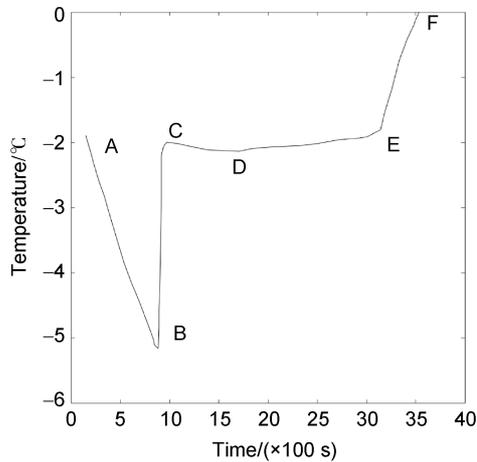


Figure 2 A typical time-temperature curve as seawater is taken through a cycle of cooling past its freezing point then heating. A–B: cool to three to four degrees below freezing point; B: beginning of nucleation, rapidly rising to C; C: supercooling is relieved; C–D: cooling continues, more ice generation, residual water salinity increases; D: cooling stops, starting to rise; E: all melting ice; E–F: liquid phase heat.

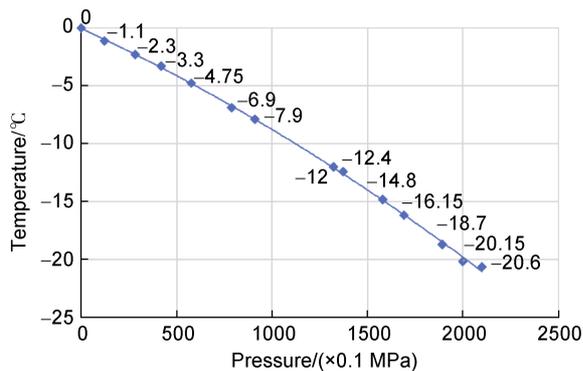


Figure 3 The relationship between the freezing point of water and pressure, data from Bridgman (1912).

chemical calculation of the Gibbs energy of seawater. Laboratory measurements of the relationship between freezing point of water and pressure were carried out by Tamman (1900). This was the first to investigate the phase diagram of H₂O at high pressure, reaching pressures of about 350 MPa. Bridgman (1912) later extended the pressure to 2050 MPa (Bridgman, 1912; Henderson and Speedy, 1987).

Henderson et al. (1987) measured the temperature of the freezing point at a pressure near 150 MPa. Some of their values are shown in Table 1.

The relationship they obtained is for freshwater. Based on high-pressure situations similar to this, Wagner and Pruss (1993), and Wagner and Pruß (2002) gave a result which is valid up to pressures of 210 MPa, but this is also for pure water only, and its low-pressure limit is based on a Clausius-Clapeyron law with relatively low accuracy. It provided a great pressure range for the freezing point of fresh water. This result has high accuracy for pure water, so

it can provide a reference for other methods (Wagner and Pruss, 1993; Wagner and Pruß, 2002).

Table 1 The variation of freezing point of freshwater with pressure

$T_f/^\circ\text{C}(\pm 0.1^\circ\text{C})$	$P/\text{MPa}(\pm 0.5\text{ MPa})$
-14.27	147.4
-10.44	114.7
-7.96	90.7
-5.10	61.4
-2.80	35.6
-0.36	4.9

Meanwhile, Fujino et al. (1974) obtained an empirical formula for the freezing point of seawater as a function of salinity and pressure, in the pressure range 1 to 10 MPa and salinity range 27‰ to 35‰, by experiment:

$$T_f(S, P) = T_f(S, 0) - 0.00759 \left(\frac{^\circ\text{C}}{\text{MPa}} \right) P, \quad (6)$$

where P is pressure, 1 MPa < P < 10 MPa.

However, Doherty et al. (1974) and Fofonoff et al. (1983) performed a thermodynamic calculation (using thermodynamic data and the Clausius-Clapeyron equation) to estimate the effect of pressure on freezing point of seawater. The Clausius-Clapeyron equation is:

$$dT_f/dP = T \left(\frac{\Delta V_f}{\Delta H_f} \right) \quad (7)$$

$\Delta V_f = V_{\text{ice}} - V_1$, V_{ice} is the molar volume at the time of ice formation, V_1 is the molar volume of water in seawater, ΔH_f is heat from melting.

They found, for fresh water at one standard atmospheric pressure, $dT_f/dP = -7.43 \times 10^{-2} \text{ }^\circ\text{C} \cdot \text{MPa}^{-1}$; for seawater of 35‰ salinity $dT_f/dP = -7.45 \times 10^{-2} \text{ }^\circ\text{C} \cdot \text{MPa}^{-1}$. They also found, $dT_f/dP = -7.51 \times 10^{-2} \text{ }^\circ\text{C} \cdot \text{MPa}^{-1}$ can be used for typical values of seawater under 5 MPa, this being close to the result of Fujino et al. (1974) (Doherty and Kester, 1974; Millero, 1978; Fofonoff and Millard, 1983).

At present, the commonly used formula for calculating the freezing point of seawater is the formula that has been found by Fofonoff and Millard (1983) on the basis of the seawater state equation of Millero and Leung (1978). In the pressure range from 0 to 5 MPa (Millero, 1978; Millero and Leung, 1978), the United Nations Educational, scientific and Cultural Organization (UNESCO) approved the equation

$$T_f = a_0 S + a_1 S^{3/2} + a_2 S^2 + bP, \quad (8)$$

where $a_0 = -0.0575 \text{ }^\circ\text{C} \cdot \text{psu}^{-1}$, $a_1 = 1.710523 \times 10^{-3} \text{ }^\circ\text{C} \cdot \text{psu}^{-3/2}$, $a_2 = -2.154996 \times 10^{-4} \text{ }^\circ\text{C} \cdot \text{psu}^{-2}$, $b = -7.53 \times 10^{-2} \text{ }^\circ\text{C} \cdot \text{MPa}^{-1}$.

There are many other methods besides these. A more accurate equation of state for seawater can be derived based

on the Gibbs thermodynamic potential, such as in Feistel and Hagen (1995), Jackett et al. (2006) and others; and many of the properties of seawater can be more accurately calculated from these equations, and the freezing point of seawater is one of them (Feistel and Hagen, 1995; Jackett et al., 2006).

For instance, Feistel et al. (1995) and Feistel (2003) calculated the variation of freezing point of seawater with salinity (S) exposed to an applied pressure (P) from the condition of thermodynamic equilibrium between seawater and ice,

$$\mu_w(S, T_f, P) = \mu_{ice}(T_f, P), \quad (9)$$

where, μ_w is chemical potential of water in seawater, μ_{ice} is chemical potential of water in ice (Feistel and Hagen, 1998) and

$$\mu_w(S, T, P) = g(S, T, P) - S \times \left(\frac{\partial g}{\partial S} \right) (T, P),$$

$$\mu_{ice}(T, P) = g_{ice}(T, P)$$

A thermodynamic potential of freshwater ice, $g_{ice}(T, P)$, has been proposed by Feistel and Hagen (1995, 1998) for the vicinity of the freezing point, derived from various properties of ice. The equilibrium between ice and water is defined by equal chemical potentials (i.e., specific free enthalpies) of both phases,

$$g(T, P) = g_w(T, P) \quad (10)$$

For the free enthalpy of water, $g_w(T, P)$, both the IAPWS-95 formulation (Wagner and Pruß, 2002) or the zero-salinity limit of the Gibbs potential of seawater (Feistel, 2003) can be used. Feistel and Wagner (2006) proposed that the freezing point temperature of water was given by the equivalent chemical potential of the solid and the liquid phase, and the calculated results showed that the temperature of the freezing point was a functional relationship with pressure (see Figure 3) (Feistel and Wagner, 2005, 2006).

$$g(T_{melt}, P) = g^L(T_{melt}, P), \quad (11)$$

where g is the Specific Gibbs energy of ice; g^L is the Specific Gibbs energy of liquid water; and T_{melt} is the melting temperature of ice.

In particular, the TEOS-10 standard used absolute salinity that is different from the practical salinity in EOS-80 (Feistel, 2008). However, both TEOS-10 and EOS-80 used the same chemical potential to calculate the freezing point. This difference in salinity causes the calculated freezing point using TEOS-10 to be smaller than that using EOS-10 (calculated by equation (8)), with the difference being 0.01 °C at a pressure of around 10 MPa and 0.05 °C at a pressure of around 20 MPa (Sun et al. 2012). For some processes with high accuracy requirements, such as those related to supercooled water (Shi et al, 2011), the sensitivities to these differences need to be evaluated in modeling studies.

The formulas listed in this section all reflect the weak

non-linear relationship between seawater freezing point and salinity (not a linear relationship, but the linear term still dominates) and the linear relationship between seawater freezing point and pressure (both of them fit the slope of freezing point temperature and pressure). And the thermodynamic background for deriving these relationships was shown in great details in Wagner and Pruß (2002) and Feistel and Wagner (2005, 2006).

3 Simulation of seawater freezing point by MITgcm and ROMs

In the numerical simulations of the ocean-ice system, especially in polar regions, the determination of the freezing point of seawater plays a crucial role. One of the important processes is the interaction of an ice shelf with the ocean. Many numerical models have already simulated this process for some ice cavities: Filchner-Ronne Ice Shelf (Gerdes et al., 1999; Jenkins and Holland, 2002; Grosfeld and Sandhäger, 2004; Jenkins et al., 2004; Grosfeld et al., 2006); the Ross Ice Shelf (Holland et al., 2003); and the Amery Ice Shelf (Williams et al., 2001, 2002). In these simulations, the determination of freezing point can affect the formation of sea ice, and affect the heat flux and fresh water flux under the ice shelf. So, the freezing point formula is one of the fundamental formulas for modeling ice shelf and ocean interaction.

In order to facilitate the model simulations, Holland et al. (1999) adapted the freezing point of seawater as a trinomial that is a linear relationship with salinity and pressure from Millero (1978). In MITgcm and ROMs, this method was used to treat the freezing point of seawater, namely:

$$T_f = aS + b + cP, \quad (12)$$

where P is the pressure at the interface; $a = -5.73 \times 10^{-2} \text{ °C} \cdot \text{psu}^{-1}$, $b = 8.32 \times 10^{-2} \text{ °C}$, $c = -7.61 \times 10^{-2} \text{ °C} \cdot \text{MPa}^{-1}$ at ROMs (Galton-Fenzi, 2009); $a = -5.75 \times 10^{-2} \text{ °C} \cdot \text{psu}^{-1}$, $b = 9.01 \times 10^{-2} \text{ °C}$, $c = -7.61 \times 10^{-2} \text{ °C} \cdot \text{MPa}^{-1}$ at MITgcm (Adcroft et al., 2008).

The biggest difference between this formula and other empirical formulas is that the nonlinear relation between salinity and freezing point is treated as a linear relationship.

4 Comparison and discussion

Hansen (1904) obtained the relationship between freezing point and salinity by a flow technique, while the one in Miyake (1939) was obtained based on a supercooling method (Kester, 1974). The results of Miyake (1939) are different from those of Knudsen (1903): The results of the freezing point of Miyake's empirical formula were 0.08 °C lower than those of Knudsen (1903) when the salinity is 35.0‰. Fujino et al. (1974) pointed out that at point C in Figure 2, 4% more ice was produced when 3 °C–4 °C of supercooling was

applied. The formation of ice would increase the salinity and decrease freezing point by about 0.08 °C for the remaining fluid (Fujino et al., 1974). So, Fujino et al. (1974) improved the experiment based on Miyaka (1939) by adding strong mixing; both these studies presented a smoothed quadratic relationship between T_f and S , which differ from each other by only 0.005 °C between 24‰ and 30‰ salinity.

The method of Millero (1976) to calculate the freezing

point temperature is very consistent with that of Doherty and Kester (1974), the difference being only about 0.001 °C. Later, MITgcm and ROMs linear formulas gave, at zero pressure, freezing points consistent with other methods with maximum differences of about 0.1 °C; within the salinity range of 25‰–40‰, the difference was smaller, being around 0.01 °C at 35‰ (see Figures 4 and 5). The results of various freezing point formulas at zero pressure are shown in Table 2.

Table 2 The variation with salinity of freezing point at zero pressure, from different formulas

$S/\text{‰}$	$T_f/^\circ\text{C} (P=0)$						
	Hansen	Miyake	Doherty and Kester	Fujino	Millero	MITgcm	ROMs
5	-0.268	-0.284	-0.275	-0.288	-0.274	-0.197	-0.203
10	-0.535	-0.569	-0.541	-0.546	-0.542	-0.485	-0.490
15	-0.803	-0.853	-0.810	-0.810	-0.812	-0.772	-0.776
20	-1.075	-1.137	-1.082	-1.079	-1.083	-1.060	-1.063
25	-1.350	-1.421	-1.359	-1.354	-1.358	-1.347	-1.349
30	-1.628	-1.706	-1.638	-1.634	-1.638	-1.635	-1.636
35	-1.910	-1.990	-1.922	-1.920	-1.922	-1.922	-1.922
40	-2.196	-2.274	-2.209	-2.211	-2.212	-2.210	-2.209

Notes: Numbers in italics indicate that the salinity is not within the applicable range of the method. Hansen (1904); Miyake (1939); Doherty and Kester (1974); Fujino et al. (1974); Millero (1978).

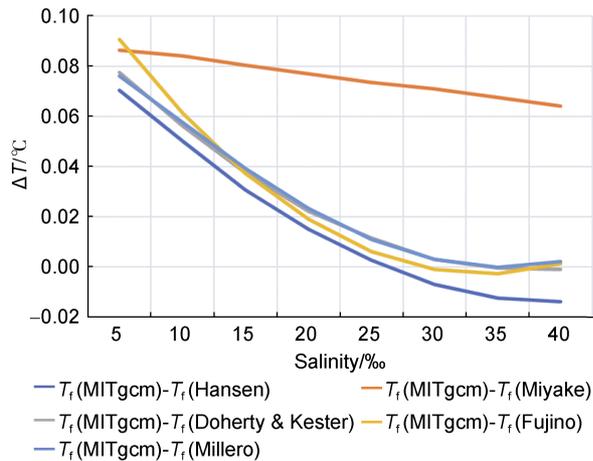


Figure 4 The difference between the freezing point at zero pressure calculated by MITgcm and those calculated by other formulas, as a function of salinity.

As the freezing point formula is a function of salinity and pressure, and is nonlinear with salinity, and the experimental data of Hansen (1904) and Bridgman (1912) were obtained with fresh water, to compare the differences with previous formulas we set S to zero in those formulas. Table 3 lists the results. From this table, the results of each formula differ very little. But the differences between them and the laboratory measurements of Bridgman (1912) and Henderson and Speedy (1987) increase gradually with an increase in pressure (Bridgman, 1912; Henderson and Speedy, 1987). When the pressure is less than 5 MPa, the formulas of Doherty and Kester (1974) and Millero (1978) have the smallest difference. The difference between them

and Henderson and Speedy (1987) is less than 0.01 °C. For a pressure between 5 and 10 MPa, the differences between Bridgman (1912) and all of the formulas are less than 0.2 °C, but the formulas used in MITgcm and ROMs are the closest to laboratory measurements. The formula used by MITgcm and ROMs is the most accurate for the pressure range of 10 to 35 MPa, with the difference being less than 0.2 °C. When the pressure is above 80 MPa, the difference is generally greater than 1 °C. When the pressure is above 200 MPa, it is 5 °C, which is too large. This is understandable because 200 MPa is beyond the range of many of the formulas.

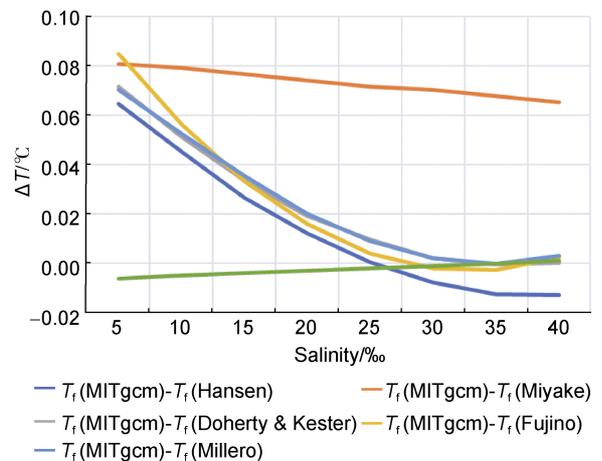


Figure 5 The difference between the freezing point at zero pressure calculated by ROMs and those calculated by other formulas, as a function of salinity.

According to the above comparison, we found that these current empirical formulas that are used in MITgcm or ROMs are reliable for calculating the freezing point temperature of seawater under high

pressure areas of ocean with the difference being less than 0.2 °C, such as Amery Ice Shelf (25 MPa) and Lake Vostok (not seawater, 35 MPa) in the Antarctic (Siegert et al., 2001).

Table 3 Variation of freezing point with pressure at zero salinity given by various formulas

$P/$ ($\times 0.1$ MPa)	$T_f/^\circ\text{C}$ ($S=0$)						
	Bridgman	Henderson and Speedy	Doherty and Kester (<50)	Fujino (<100)	Millero (<50)	MITgcm	ROMs
49		-0.360	-0.364	-0.372	-0.369	-0.373	-0.373
122	-1.100		-0.906	-0.926	-0.919	-0.928	-0.928
281	-2.300		-2.088	-2.133	-2.116	-2.138	-2.138
356		-2.800	-2.645	-2.702	-2.681	-2.709	-2.709
416	-3.300		-3.091	-3.157	-3.132	-3.166	-3.166
575	-4.750		-4.272	-4.364	-4.330	-4.376	-4.376
614		-5.100	-4.562	-4.66	-4.623	-4.673	-4.673
788	-6.900		-5.855	-5.981	-5.934	-5.997	-5.997
907		-7.960	-6.739	-6.884	-6.830	-6.902	-6.902
910	-7.900		-6.761	-6.907	-6.852	-6.925	-6.925
1147		-10.440	-8.522	-8.706	-8.637	-8.729	-8.729
1320	-12.000		-9.808	-10.019	-9.940	-10.045	-10.045
1370	-12.400		-10.179	-10.398	-10.316	-10.426	-10.426
1474		-14.270	-10.952	-11.188	-11.099	-11.217	-11.217
1580	-14.800		-11.739	-11.992	-11.897	-12.024	-12.024
1690	-16.150		-12.557	-12.827	-12.726	-12.861	-12.861
1890	-18.700		-14.043	-14.345	-14.232	-14.383	-14.383
2000	-20.150		-14.860	-15.180	-15.060	-15.220	-15.220
2100	-20.600		-15.603	-15.939	-15.813	-15.981	-15.981

Notes: Many pressure values used in this table are beyond the range of many formulas. The bold numbers represent the adjacent pressure values analyzed in the article and the freezing points calculated by formulas under the corresponding pressure. Bridgman (1912); Henderson and Speedy (1987); Miyake (1939); Doherty and Kester (1974); Fujino et al. (1974); Millero (1978).

In the above comparison, as the freezing point is calculated by the Gibbs thermodynamic potential, e.g., Feistel and Hagen (1995, 1998), Feistel (2003), Feistel and Wagner (2006), there are no simple physical formulas, and these measures are rarely used in numerical simulation, so they are not included in the comparison in this paper. However, Feistel (2003) proposed a new and extended Gibbs thermodynamic potential function of seawater, which increased the suitable pressure range for calculating the freezing point of seawater up to 50 MPa. It is compiled from an extensive set of experimental seawater data, and Feistel and Marion (2007) increased the range to 100 MPa. So, we may try to assess these formulas to high pressure areas and analyze the uncertainty in the future.

5 Conclusion

In this paper, the empirical formulas for calculating freezing point are listed. The formulas for freezing point in MITgcm

and ROMs are compared with these formulas.

The main conclusions are as follows: Firstly, some empirical formulas only consider the relationship between salinity and freezing point, which cannot be used for freezing point calculations when the pressure is not negligible; these formulas do not differ much, except for Hansen (1904) and Miyake (1939). Secondly, when the pressure is less than 5 MPa, Doherty and Kester (1974) or Millero (1978) are recommended. Thirdly, when the pressure is between 5 and 35 MPa, the formulas used in MITgcm and ROMs are the best choice, that is to say, they can be used in places of ocean where the pressure is high, such as under the Antarctic ice shelves. Fourthly, when the pressure is above 35 MPa, a difference of about 0.5 °C will be generated at 50 MPa, 1 °C at 80 MPa and 5 °C at 200 MPa. Finally, the sensitivity of the model results to these different freezing point formulas is not known at present. To quantify the sensitivity, we need to carry out sensitivity experiments by using different formulas in the models, and concern will be particularly needed when the pressure is high.

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